Chemical Kinetic Mechanism Study on Premixed Combustion of Ammonia/Hydrogen Fuels for Gas Turbine Use

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ABSTRACT

To explore the potential of ammonia-based fuel as an alternative fuel for future power generation, studies involving robust mathematical, chemical, thermofluidic analyses are required to progress towards industrial implementation. Thus, the aim of this study is to identify reaction mechanisms that accurately represents ammonia kinetics over a large range of conditions, particularly at industrial conditions. To comprehensively evaluate the performance of the chemical mechanisms, 12 mechanisms are tested in terms of flame speed, NOx emissions and ignition delay against experimental data. Freely propagating flame calculations indicate that Mathieu mechanism yields the best agreement within experimental data range of different ammonia concentrations, equivalence ratios and pressures. Ignition delay times calculations show that Mathieu mechanism and Tian mechanism yield the best agreement with data from

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shock tube experiments at pressures up to 30 atm. Sensitivity analyses were performed in to identify reactions and ranges of conditions that require optimization in future mechanism development. The present study suggests that the Mathieu mechanism and Tian mechanism are the best suited for the further study on ammonia/hydrogen combustion chemistry under practical industrial conditions. The results obtained in this study also allow gas turbine designers and modelers to choose the most suitable mechanism for combustion studies.

1 INTRODUCTION

Under the background of ever increasing energy demand and climate change issues, ammonia is a promising energy storage chemical which could be utilized to replace conventional fossil fuel. When derived from renewable sources, ammonia can be a long-term sustainable fuel capable of fulfilling some of the energy demand in isolated areas disconnected from main national grids. Compared to other fuels such as hydrogen, biofuels, shale gas, dimethyl ether, etc. ammonia can also have many advantages for its storage, delivery and distribution. For instance, ammonia contains a large hydrogen component but it does not have the same issues during storage as it can be converted into a liquid at relatively low pressure (~8 bar). Moreover, as ammonia is an important chemical used as a fertilizer, there are already well established infrastructures and experience for its storage, handling, transportation and distribution worldwide.

There have been several groups trying to utilize ammonia for practical combustion systems, mostly in internal combustion engines [1-5]. Academia has shown some development in the understanding of these systems, but this is limited [6-9]. Results show a series of challenges when utilizing this fuel including: a) lower flame

temperatures and slower kinetics; b) stability and efficiency problem; c) requirements for pre-vaporizing the ammonia ; d) pre-cracking of the molecule to improve ignition reliability and increase burning rate. NASA also identified during their XLR-99 program the need for "combustor enhancers" during start-up and idle [9]. Thus, considering hydrogen is also a carbon-free fuel and can be produced from ammonia, this research appraises ammonia/hydrogen as the fuel to be studied for the purpose of application in practical industrial system e.g. gas turbine combustion of the future[10, 11].

To utilize ammonia/hydrogen effectively, it is essential to understand better the reaction mechanisms using detailed chemical kinetic models. In addition, since computational fluid dynamics (CFD) simulations can serve as a powerful tool for analyzing and designing ammonia combustion systems, developing a CFD-based methodology alongside a detailed ammonia mechanism can help to capture more accurate information for the prediction of NOx emissions, turbulent reacting flows, combustion dynamics, ignition delays, etc. The challenging conditions in practical combustion system (e.g. gas turbine combustors) require a more specific study on the chemical progression of ammonia/hydrogen species, which is still immature for development of large scale industrial systems. Some previous studies [12-16] have developed detailed chemical mechanisms of ammonia combustion and provided agreement between measurements and simulations. For instance, Hayakawa et al. [17] provided predictions of unstretched laminar flame speed of ammonia under elevated pressure conditions with five detailed mechanisms; Kumar and Meyer [13] compared three detailed chemical mechanisms for flame speed characteristics of H_2/NH_3

combustion; Duynslaegher et al. [15] presented an improved ammonia combustion mechanism validated for the flame structure prediction of ammonia/hydrogen/oxygen/argon, etc. However, in most studies only limited chemical mechanism models, initial conditions and combustion characteristic parameters have been investigated. Therefore, mechanism studies are still not enough for more practical use, e.g. 3D CFD simulation.

Thus, there is a need to comprehensively compare the performance of different detailed ammonia combustion mechanisms in order to define the most suitable at present, simultaneously identifying the strengths and weaknesses of the mechanisms for further research. This can be resolved using numerical models to distinguish which one is capable of providing a better correlation to ammonia combustion kinetics especially under typical industrial conditions. Without any previous study in the field, it is clear that there is a great opportunity in the area to develop new mechanisms, CFD simulations, experimental setups and industrial designs.

The aim of this study is mainly to compare the performance of different detailed ammonia (NH_3) combustion mechanisms and distinguish which is most capable of representing ammonia-based fuels combustion kinetics especially under industrial conditions such as gas turbine combustor. Therefore in this study 12 recently published or tested ammonia mechanisms in literature were employed to investigate their performance on modelling ammonia-based fuel combustion. For instance, Konnov mechanism provides full implementation of kinetic data for NO formation, which has been validated by many combustion studies [13, 18]. Other mechanisms tested in this

study include Tian mechanism [19], Mathieu mechanism [14], Duynslaegher mechanism [15], Klippenstein mechanism[20], Dagaut mechanism [21], Miller mechanism [22], Lindstedt mechanism [23], ÅA mechanism [24], Mendiara mechanism [25], Mével mechanism [26] and GRI 3.0 mechanism [27]. In fact, among these detailed chemical mechanism models developed for ammonia combustion quite few of them were developed based on elevated pressure conditions. Only the model of Mathieu and Petersen was examined under pressure up to 30 atm based on shock tube experiments. The rest of the mechanisms were built up using atmospheric or low pressure conditions. Although they were not developed for conditions inside gas turbine combustors, it is meaningful to validate and expand their application range and compare the accuracy of these mechanisms for their application in gas turbines running on ammonia/hydrogen fuel blends. To comprehensively evaluate the accuracy of each detailed kinetic mechanism, unstretched flame speed, ignition delay times and NOx emissions are studied for premixed ammonia-based fuel combustion.

2 METHODOLOGY

In order to have a comparison point, experimental tests were used from relevant literature. The experimental conditions and data used in this study are shown in Table 1.

2.1 Freely Propagating Flame Modelling

Laminar flame speed is one of the most important characteristics for premixed combustion flames. It is also used as an essential parameter for detailed chemical mechanisms' verification. In this study, numerical simulations were performed using the computational code of premixed flame from Cantera [28] for the one dimensional

modelling of freely propagating laminar premixed flat flame of ammonia/hydrogen mixtures. As used in previous studies in literature [29], this model can provide analysis of unstretched flame speed, reaction rates, radical concentrations, sensitivity analyses, etc. In the model, flame speed is defined as the flame front velocity relative to the flow into the unburnt mixture [30]. Since the composition of the mixture, pressure and unburnt gas temperature will all have an effect on the laminar speed, different ammonia/hydrogen flames were modelled to comprehensively validate the performance of the existing chemical mechanisms. The numerical simulations were conducted similarly to the experimental conditions in Li et al. [31] and Hayakawa et al. [17] for the comparison of unstretched laminar flame speed values, in which different ammonia/hydrogen ratios, equivalence ratios and pressure conditions were studied.

2.2 Burner Stabilized Premixed Flame Modelling

Burner-stabilized premixed flames were assumed to be one-dimensional and can be steady enough for accurate detailed experimental measurements of species profiles, temperature, flame speed, etc. As used in [18], simulation of this kind of flame can effectively model the chemical kinetics of ammonia/hydrogen combustion process and help to interpret flame experiments. In this study, the computational code for burner-stabilized laminar premixed flame model in the Cantera software was used to predict combustion products and emissions by different kinetics mechanisms. The simulation was carried out under low pressure conditions with different ammonia/hydrogen ratios and equivalence ratios to simulate the experimental results of premixed

ammonia/hydrogen combustion provided by Duynslaegher et al. [18]. The experimental conditions are exactly performed in the simulation as shown in Table 2.

2.3 Ignition Delay Times Modelling

The ignition delay time is the time interval needed for a certain mixture to be ignited without external energy supply. Ignition delay is mainly affected by a mixture's composition, temperature and pressure. Numerical prediction of ignition delay times is helpful in understanding autoignition parameters, detailed kinetics and reduction of detailed mechanisms. In fact, as an important well-known validation technology, computational prediction of ignition delay times is usually compared with shock-tube experiments [32-34]. In this study, ignition delay times were modelled with a closed homogeneous reactor in Cantera. In this model, the ignition delay time can be defined based on different criteria such as the time at which a certain species reaches the maximum concentration or the time at which an inflection point appears in pressure or temperature profiles [14, 32, 34].

In this study, ignition delay times are extracted as the time corresponding to the steepest rate of the OH generation [14]. The model is calculated at constant volume and adiabatic conditions. In the simulation, the ammonia and oxidizer mixtures are highly diluted (98.0-99.0%) to minimize effects of viscosity, heat transfer and non-equilibrium as performed in shock-tube experimental conditions [35]. The numerical work was carried out under a wide range of pressures, temperatures and equivalence ratios to simulate the experimental results provided by Mathieu and Petersen [14]. The

mechanisms mentioned above were tested to validate their accuracy in predicting the ignition delay times.

3 RESULTS AND DISCUSSION

3.1 Flame Speed Calculation

To examine the performance of existing NH_3 combustion mechanisms for the unstretched flame speed calculation of premixed NH_3/H_2 flames, different initial NH_3 concentrations(40%~61.5%) in the fuel gas and different equivalence ratios (0.80-1.25) were simulated to compare them with results produced by Li et al.[31]. It should be noticed that the experimental data provided in the literature have not included heat losses, which should be taken into consideration for effects on flame speed predictions. However, as examined in the study performed by Kumar and Meyer [13], the effects of heat transfer to the boundaries were relatively small within most of the ranges (percent of NH_3 by energy in the fuel blends <20%) in this study especially under fuel lean conditions [31]. Thus, adiabatic conditions are assumed in the present work.

Fig. 1-3 show flame speed calculation results of different NH_3/H_2 mixtures using different chemical mechanisms. All the three NH_3/H_2 combustion results have shown that the flame speed will increase first and then decrease with the increase of equivalence ratio. Almost all the mechanisms have predicted the same trend of the flame speed with experimental data. The maximum flame speed is achieved around equivalence ratio of 1.1.

In Fig. 1, 40%NH_3/60%H_2 blend is simulated for the unstretched laminar flame speed investigation. From the results, it can be seen that most of the mechanisms have predicted slower flame speed compared to experimental data. The best predictions are

obtained by Lindstedt mechanism, Miller mechanism, Mathieu mechanism, Duynslaegher mechanism and Konnov mechanism with average relative errors of 3.99%, 5.96%, 8.53%, 8.61% and 10.08% respectively. A more detailed analysis of the results shows that in different equivalence ratio conditions the accuracy of different mechanisms varies. Near stoichiometric area (0.90<ER<1.20), the deviations of all the mechanisms are relatively larger than other zones, which indicates mechanisms for this range of equivalence ratio still need to be studied. Under fuel lean conditions (E.R.<0.90), the best predictions are obtained by Miller mechanism with an average relative error of 1.72% while Mathieu mechanism has given the best prediction under fuel rich condition(E.R.>1.20) with an average relative error of 1.38%. These results indicate that chemical reaction kinetics of this mixture are affected by equivalence ratio.

Under rich conditions, for the combustion of 40.0% NH_3 concentration in fuel, to illustrate the difference between different mechanisms, sensitivity analyses were conducted. As shown in Figs 4-7, most-sensitive reactions for the flame speed calculation of Mathieu mechanism and Miller mechanism are compared, as they produced the most accurate prediction under fuel lean and fuel rich conditions respectively. For fuel lean conditions, it can be seen from Figs 4 and 5 that the reactions $H+O_2 \Leftrightarrow O+OH$ and $H+O_2(+M) \Leftrightarrow HO_2(+M)$ have the largest impacts on the predictions of flame speed in both mechanisms. The difference between them is that these reactions play a more prominent role in Miller mechanism than in Mathieu mechanism. Even further, in both mechanisms the reaction $H_2+OH \Leftrightarrow H+H_2O$ is the second most promoting reaction for flame speed. For fuel rich conditions, Figs 6 and 7 show that promoting

reaction $H+O_2 \Leftrightarrow O+OH$ has the largest impacts on the predictions of flame speed in both mechanisms while the most inhibiting reactions in the two mechanisms are different, $N+OH \Leftrightarrow H+NO$ in Mathieu mechanism and $H+O_2(+M) \Leftrightarrow H+O_2(+M)$ in Miller mechanism. In fact, differences between rate constants of some key reactions produce also a great impact on flame speed calculation. For instance, concerning the most inhibiting reaction $H+O_2(+M) \Leftrightarrow HO_2(+M)$, the rate constant is $k=4.65\times10^{12}\cdot T^{0.44}$ in Mathieu mechanism while in Miller mechanism the value is $k=3.67\times10^{17}\cdot T^{-0.72}$. This case shows how these differences can alter the performance when predicting laminar flame speed.

Figs 2 and 3 show the flame speed calculation results for 50.0% and 61.5% of initial NH_3 concentration in the fuel blend respectively. In Fig. 2, the best predictions are obtained by Mathieu mechanism, ÅA mechanism, , Miller mechanism, Lindstedt mechanism and Dagaut mechanism with average relative errors of 3.36%, 5.38%, 9.51%, 9.72%, 9.99% respectively. In Fig. 3, the most accurate calculations are obtained by Klippenstein mechanism, Dagaut mechanism and Mathieu mechanism with average relative errors of 3.81%, 6.37%, 9.50% respectively. The simulation results from Fig. 1-3 have shown that Mathieu mechanism has the best performance (all average relative errors <10%) within the range of this study, which indicates Mathieu mechanism is capable to produce a good prediction for flame speed prediction for different ratios of NH_3/H_2 fuel mixtures. Thus, sensitivity analysis using Mathieu mechanism were performed for the combustion of 50.0% and 61.5% of initial NH_3 to illustrate the difference between combustion kinetics of different fuel mixtures, as shown in Fig. 8 and Fig. 9. The results show that both $H+O_2 \Leftrightarrow O+OH$ and $N+NH_2 \Leftrightarrow 2H+N_2$ are the most

promoting reactions while the most inhibiting reactions are different for the two different fuel mixtures. Furthermore, comparing Fig. 8 and Fig. 9 with Fig. 6, it is observed that the sensitivity of the sensitive reactions continuously change according to the proportion of NH_3 in the fuel mixture. For instance, the most sensitive reaction $H+O_2 \Leftrightarrow O+OH$ plays a more prominent role with the increase of NH_3 concentration in the fuel mixture while $H+NH_2 \Leftrightarrow H_2+NH$ plays the most inhibiting role in combustion kinetics of high NH_3 concentration mixtures.

Figs 10-12 show flame speed calculation results under different equivalence ratio conditions with detailed chemical mechanisms. As shown in the Figs, the flame speed of the NH_3/H_2 mixtures decreases with the increase of NH_3 concentration due to less amount of hydrogen atoms in the flame as the H_2 addition decreases. For stoichiometric condition, the best five performance are obtained by Mathieu mechanism, Dagaut mechanism, Miller mechanism, Klippenstein mechanism and Lindstedt mechanism. For fuel rich condition, the best agreement with experimental data was obtained by Mathieu mechanism, Dagaut mechanism, Mendiara mechanism, Tian mechanism and Klippenstein mechanism. The results show Mathieu mechanism performs with the best accuracy for flame speed prediction under stoichiometric and fuel rich cases with average relative error of 7.85% and 5.14% respectively. Meanwhile, the performance of the mechanisms used in this study for fuel lean condition is relatively poorer, in which the best predictions are obtained by Klippenstein mechanism, Dagaut mechanism, Miller mechanism, Lindstedt mechanism and Mathieu mechanism with average relative errors of 13.21%, 14.12%, 14.15%, 15.29%, 15.90% respectively. This indicates that fuel

lean combustion chemistry for NH_3/H_2 still needs to be better optimized. However, generally for all the equivalence ratio conditions in this study Mathieu mechanism shows the best and satisfying accuracy among the detailed chemical mechanisms tested.

To further study ammonia's combustion chemistry for future practical applications, elevated pressure conditions are of great significance as usually met in gas turbine operation processes. Recently Hayakawa et al. [17] studied the unstretched laminar flame speed of premixed ammonia flames at various pressures up to 0.5 MPa experimentally. Since the study of Hayakawa et al. has already compared several detailed chemical mechanisms and indicates that GRI 3.0 mechanism shows the best performance for flame speed prediction under elevated pressure conditions, here in this study Mathieu mechanism was tested and compared with GRI 3.0 mechanism under elevated pressure conditions, as shown in Fig. 13 and 14. From the results it can be seen that flame speed decreases with the increase of pressure. Although both Mathieu and GRI 3.0 mechanisms have shown good accuracy for flame speed calculation under elevated conditions, Mathieu mechanism has a better performance. Actually, although NH_3 related reactions are present in the GRI 3.0 mechanism, the ammonia chemistry in this mechanism is still not fully developed, as also mentioned in the study of Hayakawa et al. Since GRI 3.0 is still very popular in the gas turbine industry, it is necessary to notice that GRI 3.0 is not a model suitable for NH3 combustion modeling. Therefore, Mathieu mechanism already showed the best capability in simulating

ammonia/hydrogen fuel under various conditions. Thus, Mathieu mechanism is recommended for ammonia/hydrogen fuels' flame speed simulations of this study.

3.2 NOx Emission Analysis

To validate the performance of the existing chemical mechanisms for NH_3/H_2 combustion, NOx emissions and some major species concentrations were predicted against experimental data from burner-stabilized premixed flames investigated by Duynslaegher et al. [18], Figs 15-18. The initial conditions represented by point numbers are illustrated in Table 2. As shown in Fig. 15, prediction of N_2 is quite satisfying with all the mechanisms of which the relative errors are all less than 5%. For the calculation of H_2, the predictions by most mechanisms are acceptable with relative errors about 10%. For N_2O emissions, Fig. 17 shows the prediction results using different mechanisms. It can be seen that only Duynslaegher and GRI 3.0 mechanisms give best agreement with experimental data. This is because in Duynslaegher mechanism the N_2O chemistry is specifically optimized to have better accuracy. It indicates that the N_2O chemistry still needs to be improved for most of the ammonia combustion mechanisms. However, since the final concentration of N_2O in exhaust is rather low, NO_x will be regarded as the main pollutant for NH_3/H_2 flames. For exhaust NO emissions, all the chemical mechanisms tested give acceptable predictions except GRI 3.0 mechanism as shown in Fig. 18.

To develop ammonia as an alternative fuel, NO_x emissions are one of the essential concerns. Comparing flame test numbers 2, 3 and 4, it can be seen that

increase of NH_3 concentration in initial fuel leads to higher NO concentration in the burnt gas, which is mainly due to the increase of fuel-bond NO_x emissions. From flame test numbers 3, 5 and 6, it is observed a strong impact of equivalence ratio on NO yield. From fuel lean condition to fuel rich condition, a large drop in the NO concentration can be observed from ER=0.90 to ER=1.10. This indicates the fuel rich combustion can be preferred for practical industrial use of ammonia/hydrogen fuels. A comparison of flame test numbers 1, 7 and 8 reveal the effect of pressure on the formation of NO emission. From 60-120mbar, an obvious decrease of NO concentration can be observed. It should be noticed that the initial conditions in the study of Duynslaegher et al. [18] are still different from the high pressure operational conditions of practical gas turbine. As mentioned in the study of Duynslaegher et al. [18], the aim was to analyze the ammonia/hydrogen combustion chemistry for practical spark ignition engines. Nevertheless, the different pressure conditions studied by Duynslaegher have relevance to draw some of the effects of pressure that have not been studied in other related studies for NH_3/H_2 combustion. Since there is still no experimental study for ammonia/hydrogen emissions under elevated pressure conditions, this comparison can still provide essential information for NOx emission predictions.

For NO_x emission predictions, among the mechanisms tested, Tian mechanism, Klippenstein mechanism and Mendiara mechanism have performed the best accuracy with average relative errors of 5.68%, 5.69% and 5.72% respectively, while the relative error of Mathieu mechanism, which shows the best performance in flame speed calculation, shows a prediction of 23.98%. Also, relatively old mechanisms such as Miller

mechanism and Lindstedt mechanism show rather big deviations for NO_x emission predictions although they have shown fair performance for flame speed calculations. Actually, in previous literature there are studies reporting discrepancies between experimental results and these old mechanisms. For instance, Um et al. [36] over-estimated flame temperatures and NO_x emissions for non-premixed NH_3/H_2 flames, while Lee et al. [37] also claimed discrepancies among the predictions and measurements for laminar premixed NH_3/H_2 combustion using Miller mechanism and Lindstedt mechanism. This indicates that these mechanism models are not suited for future ammonia combustion studies as a great deal of improvements have already been made in chemical mechanism developments. More recent mechanisms (e.g. Tian mechanism [19] and Mendiara mechanism [25]) have been updated with much more extensive reactions for NH_3 chemistry.

To illustrate the difference between mechanisms in NO_x emission calculation, sensitivity analyses were conducted. For instance, sensitive reactions of Tian and Mathieu mechanisms for flame 1 are identified as shown in Figs 19 and 20. It can be seen that there is an obvious difference between the two models. In Tian mechanism, the most promoting reaction is $NH_2+O \Leftrightarrow HNO+H$ while $H+O_2 \Leftrightarrow OH+O$ and $NH_2+N \Leftrightarrow N_2+2H$ are the most promoting reactions in Mathieu mechanism. In Mathieu mechanism the role of N_2O species is quite important for the NO formation but not quite noticeable for Tian mechanism. These differences shown in the sensitivity analysis are mainly responsible for the discrepancy between the NO_x prediction performances of the two mechanism models. A pathway analysis of NO formation with Tian mechanism

is illustrated in Fig. 21. The major source of the NO formation comes from oxidation of HNO. As the sensitivity analysis shows, the reaction $NH_2+O \Leftrightarrow HNO+H$ plays the key role in the NO formation process. When ammonia is consumed initially with O/OH, NH_2 is produced. Then the NH_2 is mainly converted into HNO and NH. The conversion from HNO and NH to NO is mainly through the reactions $HNO+H \Leftrightarrow NO+H_2$ and $NH+O \Leftrightarrow NO+H$.

Furthermore, to gain an insight into the emission characteristics of NH_3/H_2 combustion under practical industrial conditions, simulations were carried out under a variety of pressure conditions with the fuel blend of flame test No.1 using Tian mechanism which showed the best accuracy for NO emission predictions as shown in Fig. 22. An obvious effect on NO_x emission reduction can be observed under elevated pressure conditions relevant to gas turbines. For instance, under typical pressure of 17 atm, NO_x emission concentration is as low as 0.736ppm. Thus, it indicates that the usage of NH_3/H_2 blends in gas turbines will be improved as NO_x emissions will be likely reduced under real operation conditions.

3.3 Ignition Delay Verification

To comprehensively study the performance of different chemical mechanisms for premixed combustion, ignition delay times validation studies were also conducted to compare with the experimental data by Mathieu and Petersen [14]. In [14], several up-to-date mechanisms have been tested for ignition delay time calculations of ammonia. From these studies, Mathieu mechanism has been proved to have the best accuracy under different pressure conditions. Thus, considering Tian mechanism showed the best performance for NO_x emission prediction in the previous section and it was not tested in

[14], ignition delay time calculations using Tian mechanism were compared with Mathieu mechanism as shown in Figs 23-25. Generally, under all the pressure conditions studied, both Tian mechanism and Mathieu mechanism have shown quite good accuracy for ignition delay times prediction though Mathieu mechanism performs slightly better. Specifically, under low and medium pressure conditions (1.4 and 11 atm), these two mechanisms show quite close results with each other while under high pressure condition (30 atm) Mathieu mechanism shows a better performance than Tian mechanism. This indicates that Mathieu mechanism can perform better for ignition delay time calculations under high pressure conditions.

To illustrate the difference between the chemical mechanisms for ignition chemistry, sensitivity analyses were also conducted as shown in Figs 26 and 27. Under the condition of 30 atm, equivalence ratio of 2, it can be seen that the most inhibiting reaction $NH_3+OH \Leftrightarrow NH_2+H_2O$ is the same in both mechanism. Also, promoting reactions $H+O_2 \Leftrightarrow O+OH$ and $2NH_2 \Leftrightarrow NH_3+NH$ play a prominent role in both mechanisms. A noticeable difference is that in Tian mechanism, $H+O_2 \Leftrightarrow O+OH$ plays as the most promoting reaction while $NH+O_2 \Leftrightarrow HNO+O$ is the most promoting reaction in Mathieu mechanism. Another difference is that the N_2H_2 species plays an important role in Tian mechanism. Moreover, several differences are visible between Tian mechanism and Mathieu mechanism, with the role of the N_2H_2 species being very important in Tian mechanism. These differences account for the deviation from experimental data.

4 CONCLUSION

A comprehensive comparison of different recent detailed ammonia combustion mechanisms was performed to study the premixed combustion of ammonia/hydrogen fuels. 12 detailed chemical mechanisms tested in previous literature were employed to determine their performance for the prediction of laminar flame speed, NOx emission and ignition delay times using ammonia/hydrogen blends.

First, laminar flame speed calculation under atmospheric pressure conditions, different initial NH_3 concentrations in the ammonia/hydrogen fuel mixtures and different equivalence ratios were studied using these mechanisms. Elevated pressure conditions of ammonia combustion at different equivalence ratios were also simulated with different mechanisms against the results from literature. Results show that Mathieu mechanism has the best agreement with the experimental data within the range of initial conditions tested. Second, emission analyses of diluted ammonia/ hydrogen/ oxygen/ argon flames have been modelled at different initial ammonia contents, equivalence ratios and working pressures. The best agreements of NOx emission calculation with experimental results were achieved by using Tian mechanism, Klippenstein mechanism and Mendiara mechanism. Sensitivity and pathway analyses were also carried out to identify reactions that require more attention in future development of combustion models. Simulation prediction using Tian mechanism shows industrial high pressure conditions can lead to substantial decrease of NOx emission. Finally, ignition delay time predictions for highly diluted ammonia showed that Tian mechanism and Mathieu mechanism both yielded quite good performance.

Thus, for future practical industrial use of combustion chemistry of ammonia/hydrogen fuels, both Mathieu and Tian mechanism are promising. For flame propagation, Mathieu mechanism showed the best performance while Tian mechanism can give acceptable flame speed predictions especially for fuel-rich and high ammonia concentration flames. On the other hand, though Tian mechanism showed the best performance in NOx emission prediction, Mathieu mechanism can also give acceptable NOx prediction for NH_3/H_2 fuel mixtures. The choice can depend on the specific conditions to be analyzed according to the relative error results provided in this study (Appendix A). In the future, experimental studies and optimization of these mechanisms are still needed for a deeper insight into the ammonia chemistry under practical gas turbine conditions. There will be also a need to reduce detailed ammonia/hydrogen combustion mechanisms to apply them to 3D-CFD simulation for gas turbine research.

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NOMENCLATURE

E.R.	equivalence ratio
T	temperature of unburnt mixture

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Appendix A: Average relative errors with different mechanisms

Mechanisms	Figure 1	Figure 2	Figure 3	Figure 10	Figure 11	Figure 12	Figure 15	Figure 16	Figure 17	Figure 18
Konnov	10.08%	20.54%	15.57%	22.72%	22.35%	5.14%	2.29%	19.83%	66.51%	22.85%
Duynslaegher	8.61%	16.55%	3.81%	26.76%	25.43%	9.31%	1.81%	19.37%	12.59%	15.45%
Klippenstein	25.12%	9.99%	6.37%	13.21%	15.03%	14.46%	1.54%	14.70%	43.04%	5.69%
Dagaut	16.29%	9.51%	15.52%	14.15%	7.99%	13.39%	2.07%	10.20%	74.68%	26.72%
Miller	5.96%	9.72%	24.33%	8.23%	14.12%	18.26%	2.29%	12.11%	77.18%	28.90%
Lindstedt	3.99%	5.38%	16.40%	16.74%	15.29%	12.64%	1.77%	11.44%	71.37%	12.53%
AA	19.85%	20.23%	15.15%	15.98%	16.39%	31.48%	2.12%	9.46%	72.54%	28.10%
Mendiara	26.72%	30.31%	20.53%	19.22%	17.62%	34.86%	1.59%	13.15%	50.28%	5.71%
Mével	37.93%	39.29%	37.87%	25.03%	25.18%	5.14%	1.97%	9.40%	67.64%	20.06%
GRI 3.0	38.72%	20.54%	15.57%	44.19%	35.66%	26.19%	4.45%	28.70%	16.66%	52.86%
Tian	27.10%	3.36%	9.50%	19.79%	17.94%	26.19%	1.59%	13.17%	60.95%	5.68%
Mathieu	8.53%	12.60%	38.22%	15.90%	7.85%	13.00%	2.00%	10.27%	64.51%	23.98%

Table 1 Experimental data used in this study

Fuel/Oxidizer	Specified initial conditions	Data used in this study	Reference
H_2/NH_3/air	STP, 40–66.7% NH3 in H_2 , E.R.= 0.6–1.4	Laminar flame speed	[31]
NH_3/air	T=298K, P =1-5 bar, E.R.= 0.7–1.3	Laminar flame speed	[17]
$NH_3/H_2/O_2/Ar$	T=298K, P = 60–120 mbar, E.R.=0.9–1.1	NOx emissions and combustion products	[18]
$NH_3/O_2/Ar$	T=1560–2455K, p=1.4-30bar, E.R.=0.5-2.0	Ignition delay time	[14]

Table 2 Flames inlet composition and initial conditions from [18]

No.	NH_3	H_2	O_2	Ar	E.R.	p(mbar)
1	0.25	0.05	0.21	0.48	1.00	60
2	0.24	0.07	0.21	0.47	1.00	50
3	0.22	0.10	0.21	0.46	1.00	50
4	0.21	0.13	0.21	0.45	1.00	50
5	0.22	0.10	0.24	0.43	0.90	50
6	0.22	0.10	0.20	0.48	1.10	50
7	0.25	0.05	0.21	0.48	1.00	90
8	0.25	0.05	0.21	0.48	1.00	120

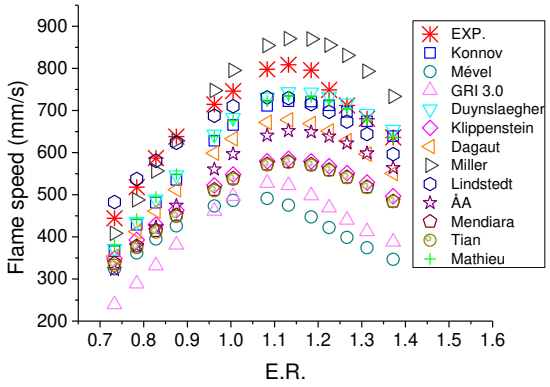

Fig. 1 Flame speed calculation of 40% NH_3 flame at normal temperature and pressure. Experiments as in [31]

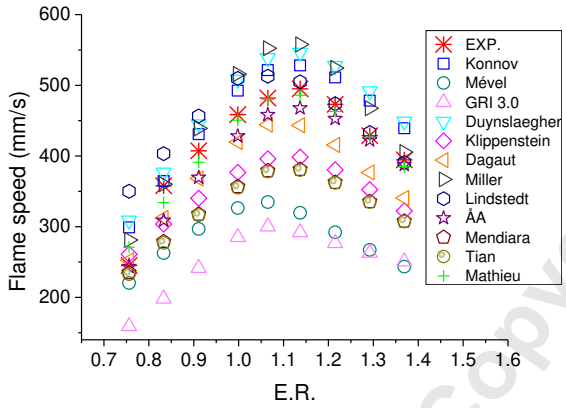

Fig. 2 Flame speed calculation of 50% NH_3 flame at normal temperature and pressure. Experiments as in [31]

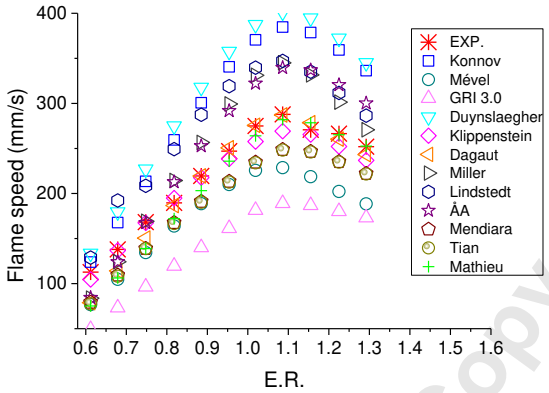

Fig. 3 Flame speed calculation of 61.5% NH_3 flame at normal temperature and pressure. Experiments as in [31]

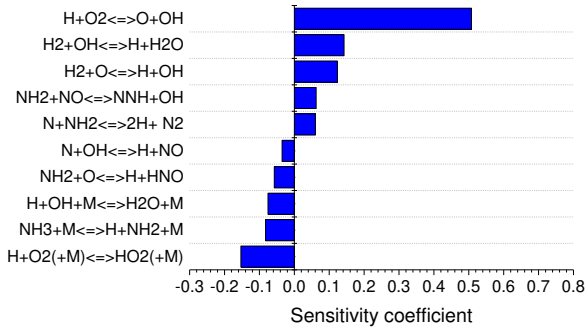

Fig. 4 Sensitivity analysis of flame speed by Mathieu mechanism (40.0%NH_3, ER=0.83)

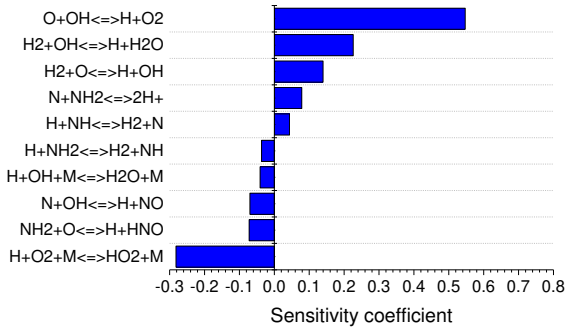

Fig. 5 Sensitivity analysis of flame speed by Miller mechanism (40.0%NH_3, ER=0.83)

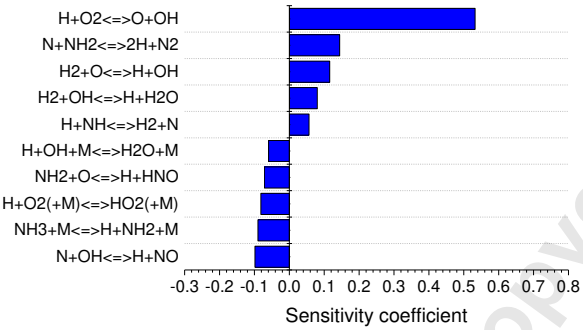

Fig. 6 Sensitivity analysis of flame speed by Mathieu mechanism (40.0%NH_3, ER=1.23)

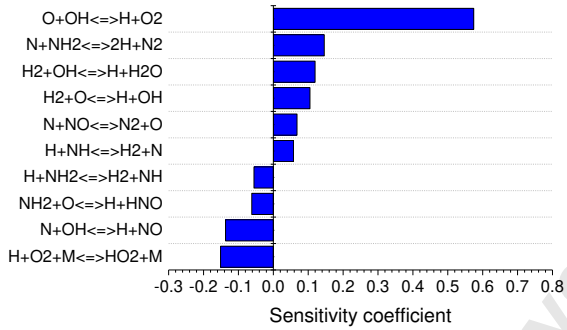

Fig. 7 Sensitivity analysis of flame speed by Miller mechanism (40.0%NH_3, ER=1.23)

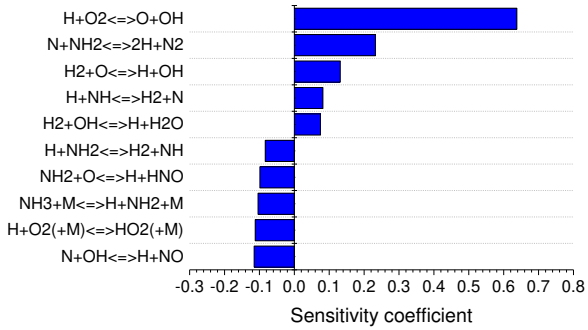

Fig. 8 Sensitivity analysis of flame speed by Mathieu mechanism (50.0%NH_3, ER=1.23)

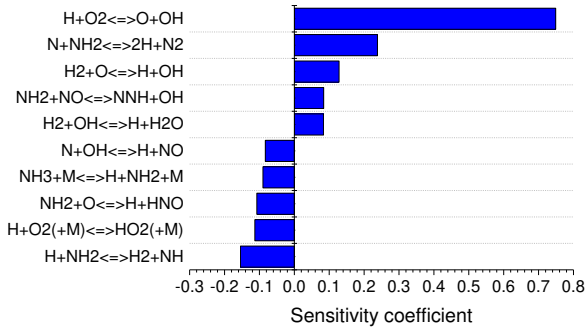

Fig. 9 Sensitivity analysis of flame speed by Mathieu mechanism (61.5%NH_3, ER=1.23)

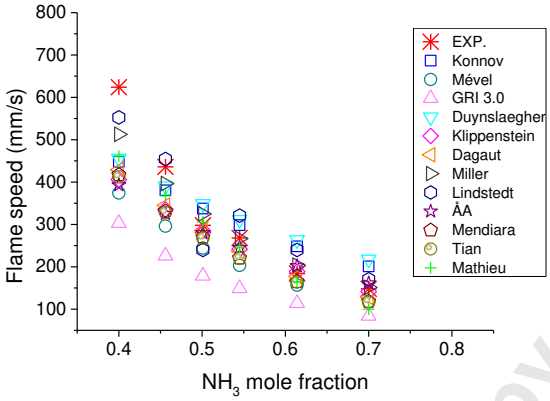

Fig. 10 Flame speed calculation of fuel lean condition (ER=0.80) at normal temperature and pressure. Experiments as in [31]

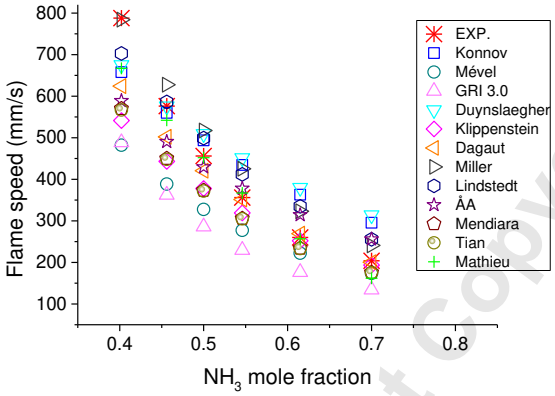

Fig. 11 Flame speed calculation of stoichiometric condition (ER=1.00) at normal temperature and pressure. Experiments as in [31]

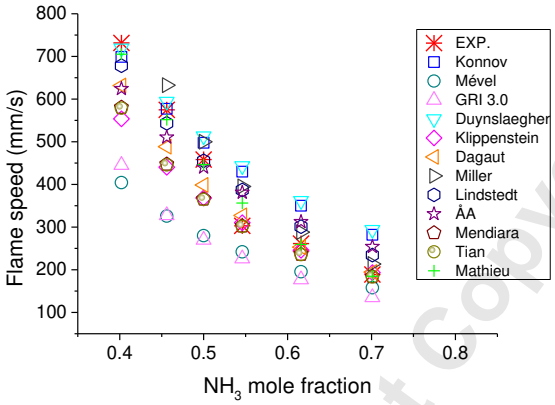

Fig. 12 Flame speed calculation of fuel rich condition (ER=1.25) at normal temperature and pressure. Experiments as in [31]

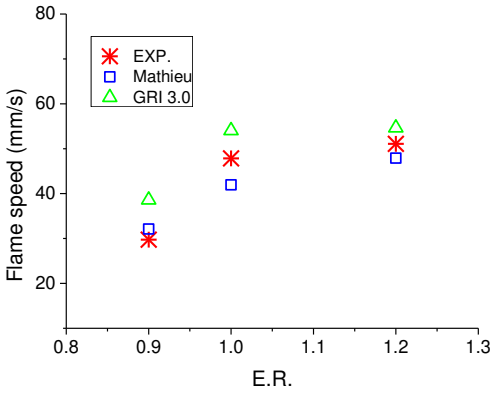

Fig. 13 Flame speed calculation of ammonia (p=0.3MPa). Experiments as in [17]

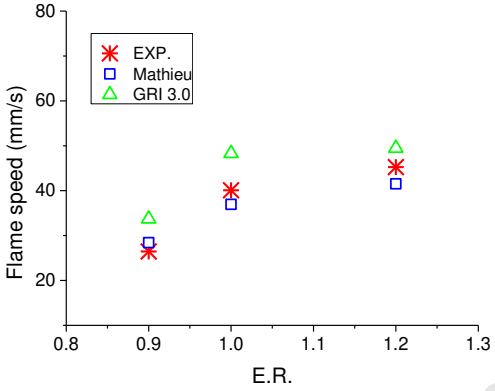

Fig. 14 Flame speed calculation of ammonia (p=0.5MPa). Experiments as in [17]

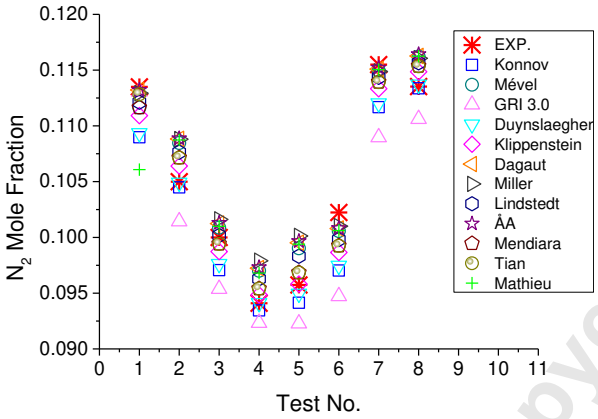

Fig. 15 Mole fraction of N_2 in burnt gas. Experiments as in [18]

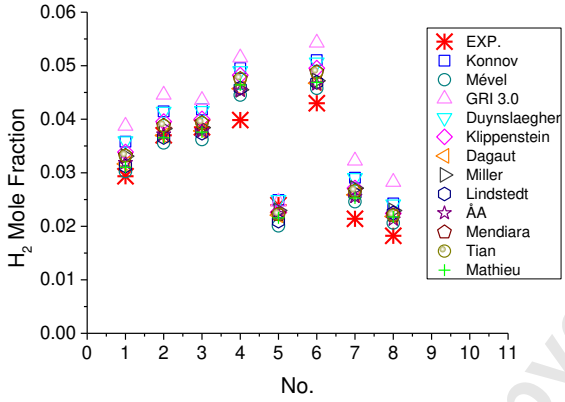

Fig. 16 Mole fraction of H_2 in burnt gas. Experiments as in [18]

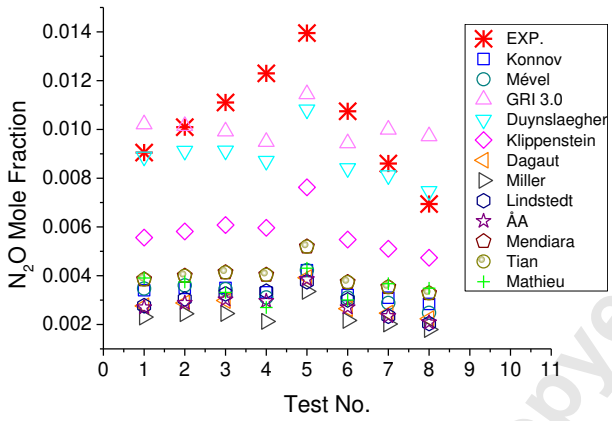

Fig. 17 Mole fraction of highest N_2O in burnt gas. Experiments as in [18]

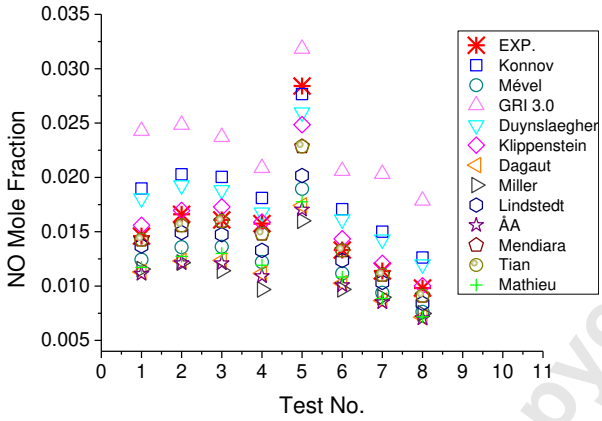

Fig. 18 Mole fraction of NO in burnt gas. Experiments as in [18]

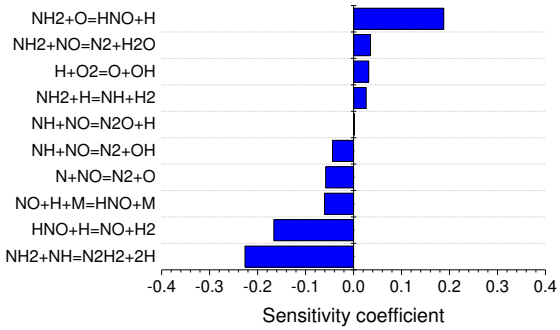

Fig. 19. Sensitivity analysis of NO by Tian mechanism (flame 1)

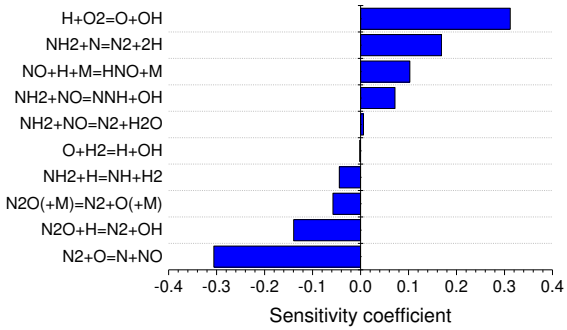

Fig. 20 Sensitivity analysis of NO by Mathieu mechanism (flame 1)

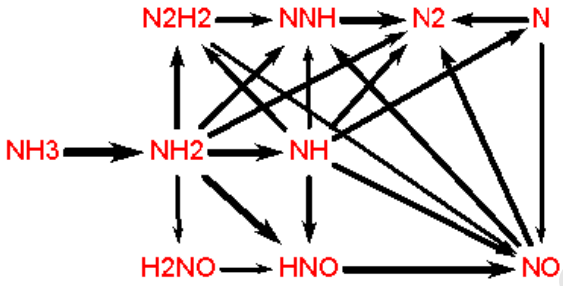

Fig. 21. Pathway of NO formation

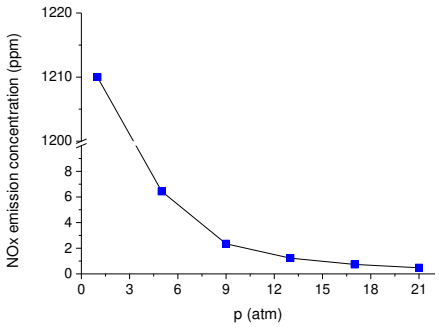

Fig. 22 NO_x emission as a function of pressure

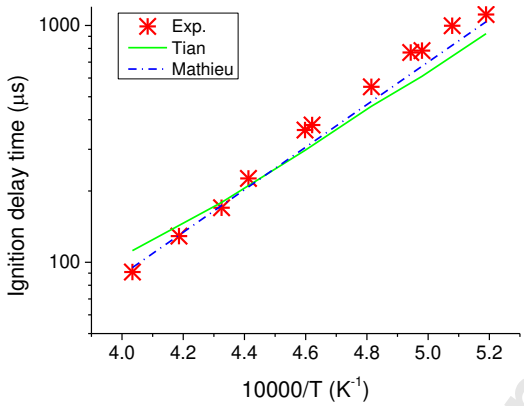

Fig. 23 Ignition delay times of NH_3 mixtures (0.4%NH_3/0.6%O_2/99%Ar). 1.4 atm. Experiments from [14]

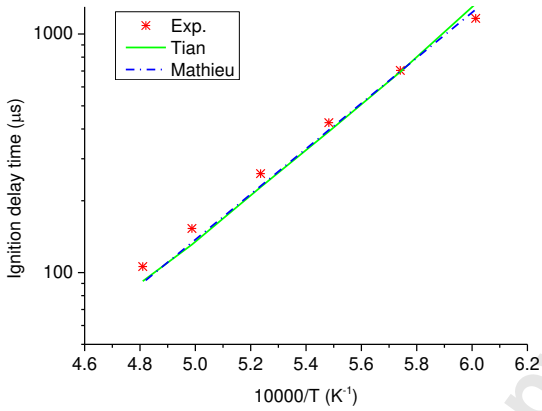

Fig. 24 Ignition delay times of NH_3 mixtures (0.4%NH_3/0.6%O_2/99%Ar). 11 atm. Experiments from [14]

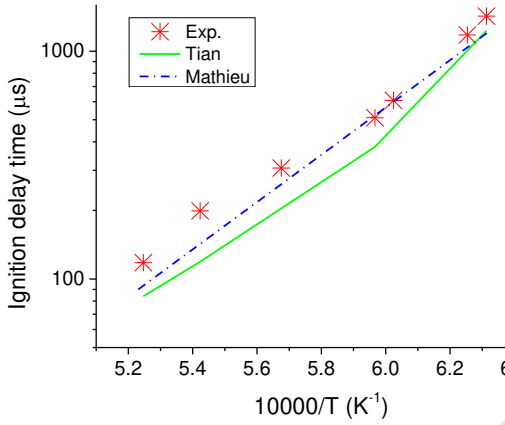

Fig. 25 Ignition delay times of NH_3 mixtures (0.4%NH_3/0.6%O_2/99%Ar). 30 atm.

Experiments from [14]

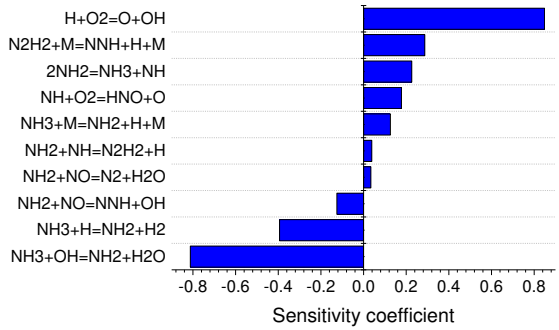

Fig. 26 Sensitivity analysis of OH by Tian mechanism (0.4%NH_3/0.6%O_2/99%Ar).

30 atm

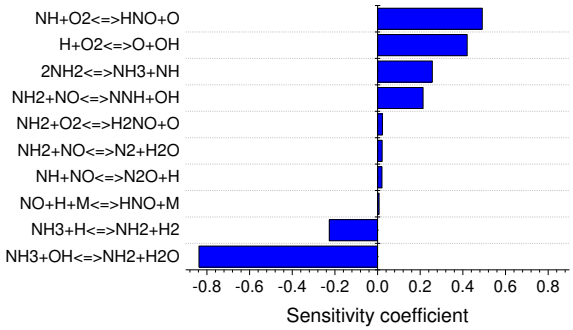

Fig. 27 Sensitivity analysis of OH by Mathieu mechanism

(0.4%NH_3/0.6%O_2/99%Ar). 30 atm